

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 987 278 A1**

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
22.03.2000 Bulletin 2000/12

(51) Int Cl.7: **C08F 8/46**

(21) Application number: **99305298.4**

(22) Date of filing: **02.07.1999**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **16.09.1998 US 153940**

(71) Applicant: **Chevron Chemical Company LLC
San Francisco, CA 94105 (US)**

(72) Inventors:
• **Harrison, James J.
Novato, California 94947 (US)**
• **Ruhe, William R. Jr.
Benecia, California 945102 (US)**

(74) Representative: **Nash, David Allan
Haseltine Lake & Co.,
Imperial House, 15-19 Kingsway
London WC2B 6UD (GB)**

(54) **Process for making a polyalkenyl derivative of an unsaturated acidic reagent**

(57) A polyalkenyl derivative of an unsaturated acidic reagent prepared by the process of reacting a polyalkene having a Mn of at least 300 with an unsaturated acidic reagent at elevated temperatures in the absence of a strong acid until at least 25% of the polyalkene is converted to a polyalkenyl derivative of an unsaturated

acidic reagent, continuing the reaction of the polyalkene with an excess of the unsaturated acidic reagent at elevated temperatures in the presence of a strong acid to convert at least some of the unreacted polyalkene to additional polyalkenyl derivative of an unsaturated acidic reagent, and removing the unreacted unsaturated acidic reagent.

EP 0 987 278 A1

Description

[0001] The present invention relates to an improved process for making a polyalkenyl derivative of an unsaturated acidic reagent.

BACKGROUND OF THE INVENTION

[0002] Previously, it has been shown that the addition of a strong acid (such as sulfonic acid) to the process of preparing a polyalkenyl derivative of an unsaturated acidic reagent results in a faster rate of reaction, higher conversion, less tar, and a lower succinic ratio.

[0003] U.S. Patent No. 3,819,660, titled "Alkenylsuccinic Anhydride Preparation," discloses the suppression of fumaric acid sublimation and tar formation during reaction of a 168 to 900 molecular weight alkene with maleic anhydride and increased yield of alkenylsuccinic anhydride by using a catalytic amount of p-alkylbenzenesulfonic acid.

[0004] U.S. Patent No. 4,235,786, titled "Process for Producing Oil-Soluble Derivatives of Unsaturated C₄-C₁₀ Dicarboxylic Acid Materials," discloses the Ene reaction of an unsaturated C₄-C₁₀ dicarboxylic acid and a C₃₀-C₇₀₀ olefin carried out in the presence of an oil-soluble, strong organic acid having a pK_a of less than 4, such as sulfonic acid.

[0005] U.S. Patent No. 5,777,025, titled "Process for Preparing Polyalkenyl Substituted C₄ to C₁₀ Dicarboxylic Acid Producing Materials," discloses a process for preparing a polyalkylene derivative of a monounsaturated C₄ carboxylic acid by running the reaction in the presence of a sediment-inhibiting amount of an oil-soluble hydrocarbyl substituted sulfonic acid.

[0006] European Patent Application 0 542 380 A1, titled "Process for the preparation of polyalkenyl derivatives of unsaturated dicarboxylic acid materials," discloses a process for the preparation of a polyalkenyl derivative of a monoethylenically unsaturated C₄-C₁₀ dicarboxylic acid material wherein the ratio of dicarboxylic acid moieties per polyalkenyl chain is less than 1.2:1. That process comprises reacting a polyalkene having a Mn in the range of 950 to 5000 with a monoethylenically unsaturated C₄-C₁₀ dicarboxylic acid material in a mole ratio of greater than 1:1 at a temperature in the range of 150° to 260°C in the presence of a polyaddition-inhibiting amount of a sulfonic acid.

[0007] In all of these applications, the sulfonic acid is added at the beginning of the reaction.

SUMMARY OF THE INVENTION

[0008] The present invention provides an improved process for the preparation of a polyalkenyl derivative of an unsaturated acidic reagent. That process is based upon the discovery that starting the reaction without the strong acid, then adding that strong acid later results in a shorter residence time to obtain the same conversion.

[0009] The process comprises the steps of:

- (a) reacting a polyalkene having a Mn of at least 300 with an unsaturated acidic reagent at elevated temperatures in the absence of a strong acid until at least 25% of the polyalkene is converted to a polyalkenyl derivative of an unsaturated acidic reagent;
- (b) continuing the reaction of the polyalkene with an excess of the unsaturated acidic reagent at elevated temperatures in the presence of a strong acid to convert at least some of the unreacted polyalkene to additional polyalkenyl derivative of an unsaturated acidic reagent; and
- (c) removing the unreacted unsaturated acidic reagent.

[0010] Preferably, the reaction medium is cooled as soon as the unreacted unsaturated acidic reagent has been removed.

[0011] Preferably, in step (a), the polyalkene is reacted with an unsaturated acidic reagent in the absence of a strong acid until between 25% and 80% of the polyalkene is converted to a polyalkenyl derivative of an unsaturated acidic reagent. More preferably, the polyalkene is reacted with an unsaturated acidic reagent in the absence of a strong acid until between 60% and 75% of the polyalkene is converted to a polyalkenyl derivative of an unsaturated acidic reagent.

[0012] Preferably, the polyalkene is a polybutene. More preferably, the polybutene is a polyisobutene, most preferably wherein at least 50% of said polyisobutene has methylvinylidene end groups. Preferably, the polyalkene has a Mn of from 500 to 2500.

[0013] Preferably, the unsaturated acidic reagent is maleic anhydride.

[0014] Preferably, the mole ratio of unsaturated acidic reagent to polyalkene is at least 1.0:1.

[0015] Preferably, the strong acid is an oil-soluble, strong organic acid, having a pK_a of less than about 4. More preferably, it is a sulfonic acid, such as an alkyl aryl sulfonic acid, wherein the alkyl group has from 4 to 30 carbon atoms. Preferably, the sulfonic acid is present in an amount in the range of from 0.0025% to 1.0% based on the total weight of polyalkene.

DETAILED DESCRIPTION OF THE INVENTION

[0016] In its broadest aspect, the present invention involves the discovery that, in the process for the preparation of a polyalkenyl derivative of an unsaturated acidic reagent, if one starts the reaction without the strong acid, then adds that acid later in the process, one achieves results in a shorter residence time at the same conversion.

[0017] The process comprises the steps of:

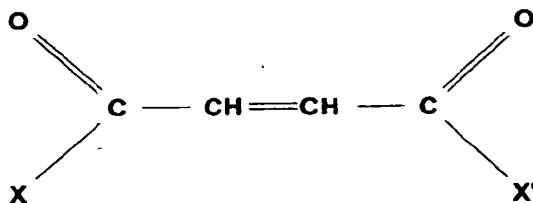
- (a) reacting a polyalkene having a Mn of at least 300 with an unsaturated acidic reagent at elevated temperatures in the absence of a strong acid until at least 25% of the polyalkene is converted to a polyalkenyl derivative of an unsaturated acidic reagent;
- (b) continuing the reaction of the polyalkene with an excess of the unsaturated acidic reagent at elevated temperatures in the presence of a strong acid to convert at least some of the unreacted polyalkene to additional polyalkenyl derivative of an unsaturated acidic reagent; and
- (c) removing the unreacted unsaturated acidic reagent.

THE POLYALKENE

[0018] The polyalkene can be a polymer of a single type of olefin or it can be a copolymer of two or more types of olefins. Preferably, the polyalkene is a polybutene, more preferably a polyisobutene, and most preferably a polyisobutene wherein at least 50% of the polyisobutene has methylvinylidene end groups. Preferably, the polyalkene has a number average molecular weight (Mn) of from 500 to 2500.

THE UNSATURATED ACIDIC REAGENT

[0019] The term "unsaturated acidic reagent" refers to maleic or fumaric reactants of the general formula:



wherein X and X' are the same or different, provided that at least one of X and X' is a group that is capable of reacting to esterify alcohols, form amides, or amine salts with ammonia or amines, form metal salts with reactive metals or basically reacting metal compounds and otherwise function as acylating agents. Typically, X and/or X' is -OH, -O-hydrocarbyl, -OM⁺ where M⁺ represents one equivalent of a metal, ammonium or amine cation, -NH₂, -Cl, -Br, and taken together X and X' can be -O- so as to form an anhydride. Preferably, X and X' are such that both carboxylic functions can enter into acylation reactions. Maleic anhydride is a preferred unsaturated acidic reactant. Other suitable unsaturated acidic reactants include electron-deficient olefins such as monophenyl maleic anhydride; monomethyl, dimethyl, monochloro, monobromo, monofluoro, dichloro and difluoro maleic anhydride, N-phenyl maleimide and other substituted maleimides; isomaleimides; fumaric acid, maleic acid, alkyl hydrogen maleates and fumarates, dialkyl fumarates and maleates, fumaronilic acids and maleanic acids; and maleonitrile, and fumaronitrile.

THE STRONG ACID

[0020] The term "strong acid" refers to an acid having a pK_a of less than about 4. Preferably, the strong acid is an oil-soluble, strong organic acid. More preferably, the strong acid is a sulfonic acid. Still more preferably, the sulfonic acid is an alkyl aryl sulfonic acid. Most preferably, the alkyl group of said alkyl aryl sulfonic acid has from 4 to 30 carbon atoms.

[0021] Preferably, the sulfonic acid is present in an amount in the range of from 0.0025% to 1.0% based on the total weight of polyalkene.

THE PROCESS FOR PREPARING POLYALKENYL DERIVATIVES

[0022] In the preparation of the polyalkenyl derivative, the mole ratio of unsaturated acidic reagent to polyalkene is preferably at least 1.0:1. More preferably, that mole ratio is from 1.0:1 to 4.0:1.

[0023] Preferably, the unsaturated acidic reagent is added over a short time period (such as from ½ to 3 hours) instead of all at once, in order to get high conversion and minimize sediment.

[0024] In the first step of the process, the polyalkene is reacted with an unsaturated acidic reagent at elevated temperatures in the absence of a strong acid until at least 25% of the polyalkene is converted to a polyalkenyl derivative of an unsaturated acidic reagent. Preferably, between 25% and 80% of the polyalkene is converted to polyalkenyl derivative in the absence of a strong acid. More preferably, between 60% and 75% of the polyalkene is converted to polyalkenyl derivative in the absence of a strong acid.

[0025] One can measure the % conversion of the reaction by any means known to someone skilled in the art. For example one method for measuring the % actives is to elute a sample on a column of silica gel, alumina, or other suitable adsorbant using hexane or other non polar solvent. In this case the unreacted polybutene is eluted by the hexane and the PIBSA is retained on the column. After the hexane is evaporated from the sample that is eluted, the unreacted polybutene is weighed. Then subtraction of the weight of the unreacted polybutene from the total weight of sample added to the column, and then dividing this by the total weight of sample and multiplication by 100, gives the % actives. The % conversion is calculated from the weight % actives using the procedure described in U. S. patent 5,625,004.

[0026] In the second step, the reaction is continued with an excess of unsaturated acidic reagent at elevated temperatures in the presence of a strong acid to convert at least some of the unreacted polyalkene to additional polyalkenyl derivative of an unsaturated acidic reagent.

[0027] The temperature of the reaction in the first and second step can vary over a wide range. Preferably, the temperature is in the range of from 180° to 240°C. The pressure can be atmospheric, sub-atmospheric, or super-atmospheric. Preferably, the pressure is super-atmospheric.

[0028] In the third step, the unreacted unsaturated acidic reagent is removed. Preferably, the reaction medium is cooled as soon as the unreacted unsaturated acidic reagent has been removed.

EXAMPLES

[0029] The invention will be further illustrated by the following examples, which set forth particularly advantageous method embodiments. While the Examples are provided to illustrate the present invention, they are not intended to limit it.

COMPARATIVE EXAMPLES A AND B

SULFONIC ACID ADDITION PRIOR TO POLYBUTENE HEATING

[0030] 4000 grams of high methylvinylidene polyisobutene (BASF Glissopal 1000 in Comparative Example A and Glissopal 2300 in Comparative Example B) was added to a 12 liter stainless steel reactor in the following manner. First, approximately half of the PIB charge was added to the reactor. Then, a C₄-C₃₀ alkyl sulfonic acid was added dropwise to the reactor. Then, the remaining PIB was added to the reactor. The reactor was heated to 232°C under a nitrogen atmosphere. Stirring was at approximately 600 rpm. Once the reactor reached 232°C, the reactor was held at these conditions for PIB dehydration for 15 minutes. After dehydration, the reactor was pressured to approximately 25 psia using nitrogen. Once the reactor reached this pressure, the maleic anhydride was added at a constant rate (701 grams over 1.0 hour in Comparative Example A and 535 grams over 1.2 hour in Comparative Example B). At the end of the maleic anhydride addition, the reactor conditions were held for a period of six hours for Comparative Example A and three hours for Comparative Example B in order to develop data on how conversion varies with time. Samples were taken every hour during the hold period. (In an optimized reaction, the reaction would have been terminated once the desired conversion has been reached.) After the hold period, the reactor was depressurized to approximately atmospheric pressure in approximately 35 minutes. Next, vacuum was slowly applied, and the reactor depressurized to less than 50 mm mercury (absolute) over approximately 37 minutes. Once the reactor pressure reached less than 50 mm mercury (absolute), this condition was held for 53 minutes. At the end of this hold period, the vacuum was shut off, and the reactor was pressurized to approximately atmospheric pressure. The remaining reaction product was transferred to a pressure filter, and filtered. The filtered product was analyzed for saponification number and % actives.

EXAMPLES 1 AND 2

SULFONIC ACID AFTER POLYBUTENE HEATING

[0031] Examples 1 and 2 were the same as Comparative Examples A and B, respectively except that the sulfonic acid was added to the reaction mixture after at least 25% conversion.

Example	PIB Conversion when Strong Acid added (%)	PIB Conversion (%)					
		1 HR	2 HR	3 HR	4 HR	5 HR	6 HR
A 1	0	52.8	78.9	86.8	90.0	91.5	92.4
	67.6%	67.6	83.4	89.2	91.2	92.3	93.1
B 2	0	56.0	80.9	89.0			
	66.6%	66.6	84.0	89.7			

[0032] Comparing Comparative Example A with Example 1, or Comparative Example B with Example 2, shows that one can achieve similar conversions in less time, or higher conversions in the same time, by adding the strong acid after a significant amount PIB has already been converted.

[0033] While the present invention has been described with reference to specific embodiments, this application is intended to cover those various changes and substitutions that may be made by those skilled in the art without departing from the spirit and scope of the appended claims.

Claims

1. A process for the preparation of a polyalkenyl derivative of an unsaturated acidic reagent, said process comprising the steps of:
 - (a) reacting a polyalkene having a Mn of at least 300 with an unsaturated acidic reagent at elevated temperatures in the absence of a strong acid until at least 25% of the polyalkene is converted to a polyalkenyl derivative of an unsaturated acidic reagent;
 - (b) continuing the reaction of said polyalkene with an excess of said unsaturated acidic reagent at elevated temperatures in the presence of a strong acid to convert at least some of the unreacted polyalkene to additional polyalkenyl derivative of an unsaturated acidic reagent; and
 - (c) removing the unreacted unsaturated acidic reagent.
2. A process according to Claim 1, wherein the reaction medium is cooled as soon as the unreacted unsaturated acidic reagent is removed.
3. A process according to Claim 1, wherein in step (a), the polyalkene is reacted with an unsaturated acidic reagent in the absence of a strong acid until between 25% and 80% of the polyalkene is converted to a polyalkenyl derivative of an unsaturated acidic reagent.
4. A process according to Claim 3, wherein in step (a), the polyalkene is reacted with an unsaturated acidic reagent in the absence of a strong acid until between 60% and 75% of the polyalkene is converted to a polyalkenyl derivative of an unsaturated acidic reagent.
5. A process according to Claim 1 wherein said polyalkene is a polybutene.
6. A process according to Claim 5 wherein said polybutene is a polyisobutene.
7. A process according to Claim 6 wherein at least 50% of said polyisobutene has methylvinylidene end groups.
8. A process according to Claim 1 wherein said polyalkene has a Mn of from 500 to 2500.

9. A process according to Claim 1 wherein said unsaturated acidic reagent is maleic anhydride.
10. A process according to Claim 1 wherein the mole ratio of unsaturated acidic reagent to polyalkene is at least 1.0:1.
- 5 11. A process according to Claim 1 wherein said strong acid is an oil-soluble, strong organic acid.
12. A process according to Claim 11 wherein said strong acid is a sulfonic acid.
13. A process according to Claim 12 wherein said sulfonic acid is an alkyl aryl sulfonic acid.
- 10 14. A process according to Claim 13 wherein said alkyl group of said alkyl aryl sulfonic acid has from 4 to 30 carbon atoms.
- 15 15. A process according to Claim 12 wherein the sulfonic acid is present in an amount in the range of from 0.0025% to 1.0% based on the total weight of polyalkene.

20

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 30 5298

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
D,Y	US 5 777 025 A (J. R. SPENCER) 7 July 1998 (1998-07-07) * column 4, line 11 - column 5, line 57 * * column 6, line 50 - column 7, line 67 * * column 8, line 33 - column 9, line 11; claims 1-20 *	1-15	C08F8/46
Y	WO 94 02571 A (CHEVRON RESEARCH AND TECHNOLOGY COMPANY) 3 February 1994 (1994-02-03) * page 8, line 3 - page 9, line 21 * * page 10, line 16 - page 11, line 33; claims 1-13 *	1-15	
Y	US 4 883 886 A (C. HUANG) 28 November 1989 (1989-11-28) * the whole document *	1-15	
A	EP 0 014 288 A (EXXON RESEARCH AND ENGINEERING COMPANY) 20 August 1980 (1980-08-20) * page 5, line 31 - page 6, line 17 * * page 6, line 28 - page 7, line 30 * * page 7, line 34 - page 9, line 13; claims 1-5 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C08F
D,A	EP 0 542 380 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 19 May 1993 (1993-05-19) * page 3, line 24 - page 4, line 48; claims 1-10 *	1	
A	WO 94 02572 A (CHEVRON RESEARCH AND TECHNOLOGY COMPANY) 3 February 1994 (1994-02-03) * page 7, line 27 - page 9, line 12 * * page 10, line 1 - page 11, line 17; claims 1-13 *	1	
		-/--	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22 December 1999	Examiner Permentier, W
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons S : member of the same patent family, corresponding document	

EPO FORM 1503 (03-02) (PctCo)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 30 5298

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	FR 2 354 347 A (THE LUBRIZOL CORPORATION) 6 January 1978 (1978-01-06) * page 1, line 19 - page 2, line 8 * * page 3, line 22 - page 5, line 10 * * page 5, line 19 - page 6, line 13; claims 1-11 *	1	
A	EP 0 082 601 A (BP CHEMICALS LTD.) 29 June 1983 (1983-06-29) * claims 1-6 *	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22 December 1999	Examiner Permentier, W
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 30 5298

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

22-12-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5777025 A	07-07-1998	CA 2197105 A US 5891953 A	10-08-1997 06-04-1999
WO 9402571 A	03-02-1994	US 5286799 A CA 2119012 A DE 69318528 D DE 69318528 T EP 0605715 A JP 7501832 T	15-02-1994 03-02-1994 18-06-1998 10-09-1998 13-07-1994 23-02-1995
US 4883886 A	28-11-1989	NONE	
EP 14288 A	20-08-1980	AR 226046 A BR 7907973 A CA 1148557 A JP 1395710 C JP 55102605 A JP 62003162 B	31-05-1982 21-10-1980 21-06-1983 24-08-1987 06-08-1980 23-01-1987
EP 542380 A	19-05-1993	AU 653650 B AU 2836492 A CA 2082913 A CN 1072417 A CZ 283113 B HU 214192 B JP 5230131 A	06-10-1994 20-05-1993 16-05-1993 26-05-1993 14-01-1998 28-01-1998 07-09-1993
WO 9402572 A	03-02-1994	US 5625004 A CA 2119011 A DE 69318529 D DE 69318529 T EP 0605716 A JP 7501833 T	29-04-1997 03-02-1994 18-06-1998 17-09-1998 13-07-1994 23-02-1995
FR 2354347 A	06-01-1978	US 4110349 A CA 1082204 A GB 1533819 A JP 52151120 A MX 148822 A	29-08-1978 22-07-1980 29-11-1978 15-12-1977 24-06-1983
EP 82601 A	29-06-1983	JP 58093706 A US 4472588 A	03-06-1983 18-09-1984

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82